The Chlorides of Ortho-sulpho-benzoic Acid

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

MARION BYRD HOPKINS

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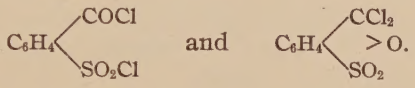
ACKNOWLEDGMENT.

The investigation described in the following pages was undertaken at the suggestion of Professor Remsen, and carried out under his supervision. I gladly avail myself of this opportunity to express my sincere thanks to him. I wish, also, to thank Doctors Morse, Jones, Gilpin, Acree, Lovelace, Reid and Frazer for the valuable instruction and encouragement received from them during my course as a student in the Johns Hopkins University. I also feel under obligations to Dr. C. A. Rouiller for kindly advice and suggestions.

HISTORICAL.

Chlorides of Ortho-sulphobenzoic Acid.

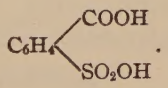
In 1891, Remsen and Coates[1] found that the dichloride of ortho-sulphobenzoic acid yielded with aniline two isomeric anilides, and they concluded that the chloride consisted of a mixture of a symmetrical and an unsymmetrical chloride of the formulas



One of these, Remsen and Kohler[2] isolated in fairly pure crystalline form in 1892 and called it the symmetrical chloride. Three years later Remsen and McKee[3] obtained the pure product melting at 79.5°. Remsen and Saunders[4] isolated in crystalline form what they supposed to be the pure unsymmetrical form with a melting point of 21.5°. List and Stein[5] showed that this crystalline substance consisted of a molecular mixture or unstable compound of the two chlorides and that the pure low-melting chloride melts at 40°.

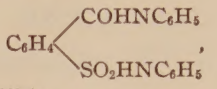
In attempts to determine which of the two chlorides has the symmetrical and which the unsymmetrical structure, the action of various reagents upon them has been studied. The work has been done largely by Remsen and his students working in this laboratory. Briefly stated the most important results of these investigations are as follows:

1. *Action with Water.*[6]—Both chlorides yield ortho-sulphobenzoic acid,

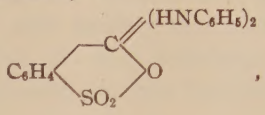


[1] Am. Ch. J., 17, 311.
[2] Ibid., 17, 330.
[3] Ibid., 18, 806.
[4] Ibid., 17, 311.
[5] Ber. d. chem. Ges., 31, 1653.
[6] Am. Ch. J., 17, 350; 18, 798; 30, 255.

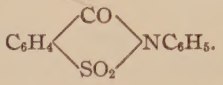
2. Action with Aniline.[1]—According to List and Stein, both chlorides yield the symmetrical anilide,



the unsymmetrical anilide,

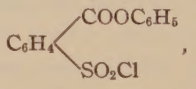


and the anil,

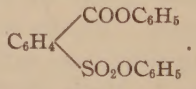


Remsen and Holmes[2] find that when the high-melting chloride is treated with aniline in the presence of water, no trace of the unsymmetrical anilide is formed, the products being the symmetrical anilide and the anil. On the other hand, when the low-melting chloride is treated in the same way the products are the two anilides and no anil.

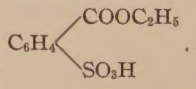
3. Action with Phenol.[3]—Both chlorides give the phenyl ester chloride of ortho-sulphobenzoic acid,



and the diphenyl ester of ortho-sulphobenzoic acid,

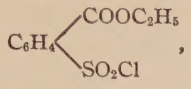


4. Action with Alcohols.[4]—The high-melting chloride does not react with alcohol until heated. It then yields the acid ethyl ester of ortho-sulphobenzoic acid,



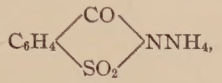
[1] Am. Ch. J., **17**, 311; **18**, 804; Ber. d. chem. Ges., **31**, 1648.
[2] Am. Ch. J., **30**, 273.
[3] Ibid., **17**, 352; **30**, 292; Ber. d. chem. Ges., **31**, 1661.
[4] Am. Ch. J., **11**, 341; **18**, 825; **30**, 268; Ber. d. chem. Ges., **31**, 1659.

The low-melting chloride gives the ester chloride,

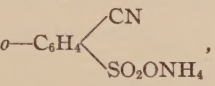


and then in turn the acid ester.

5. Action with Ammonia.[1]—The high-melting chloride gives ammonium benzoic sulphimide,

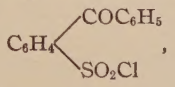


and the low-melting chloride the ammonium salt of ortho-cyanbenzene sulphonic acid,

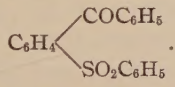


and also a little of the sulphimide.

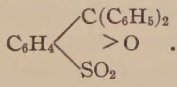
6. Action with Benzene and Aluminium Chloride.[2]—Both chlorides give ortho-benzoylbenzenesulphone chloride,



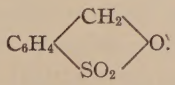
and also ortho-benzoyldiphenylsulphone,



Under conditions which have not yet been determined, a mixture of the two chlorides gives a product of the structure



7. Action with Reducing Agents.[3]—The high-melting chloride gives sulphobenzid,

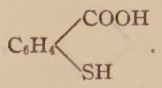


[1] Am. Ch. J., **17**, 351; **18**, 819; **30**, 262; Ber. d. chem. Ges., **31**, 1656.

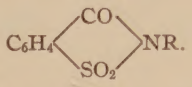
[2] Am. Ch. J., **17**, 354; **18**, 806; **45**, 605; **35**, 486; Ber. d. chem. Ges., **29**, 2295; **31**, 1664.

[3] Ber. d. chem. Ges., **31**, 1664; Am. Ch. J., **30**, 254.

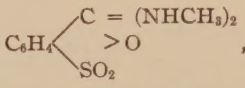
The low-melting chloride gives thiosalicylic acid,



8. Action with Amines.[1]—The action of methyl-, ethyl- and dimethylamine has been studied. The high-melting chloride gives an ester of benzoic sulphinide,



The low-melting chloride gives this same ester together with an infusible diamide to which the unsymmetrical structure,



is assigned. No evidence is given that this compound has not the symmetrical structure.

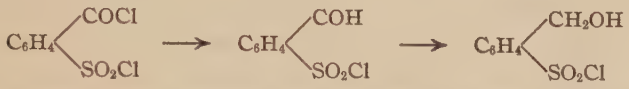
9. Light Absorption.[2]—Of the two chlorides, Scheiber and Knothe have shown that the low-melting form shows absorption of the same nature as the acid itself, while the high-melting form is much more transparent.

Relying upon the reactions of the chlorides with ammonia and aniline Remsen concludes that the high-melting chloride has the symmetrical structure and the low-melting chloride the unsymmetrical structure. He says, however, "It must be confessed that the case is a difficult one to deal with, for the reason that, with some reagents, both chlorides give the same products, and these sometimes have the symmetrical and sometimes the unsymmetrical structure." List and Stein hold that the facts do not justify any conclusion in regard to the structure of the chlorides. They think the fact that, upon reduction, the high-melting chloride yields sulphobenzid and the low-melting chloride thiosalicylic acid is evidence in favor of the unsymmetrical formula for the high-melting, and the symmetrical formula for the low-melting

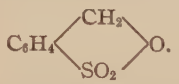
[1] Am. Ch. J., **30**, 277.

[2] Ber. d. chem. Ges., **45**, 2262 (1912); **46**, 2366 (1913).

chloride. Remsen here raises the question, "Can the reactions of the two chlorides with reducing agents be explained in any other plausible way than that adopted by List and Stein?" He thinks that by a consideration of the idea that the –COCl group is more easily reduced than the $-SO_2Cl$ group they can be. According to this the symmetrical chloride should first yield an aldehyde and then an alcohol, thus:



The alcohol would easily lose hydrochloric acid and give the corresponding anhydride, sulphobenzid,



According to this the formation of sulphobenzid from a symmetrical chloride appears possible. As regards the formation of thiosalicylic acid from the low-melting chloride, the explanation is offered that before the reduction could be effected the chloride would be converted partly into the anhydride and partly into the acid. The reduction of these would be likely to give thiosalicylic acid.

The idea, however, that the –COCl group would be reduced completely to the alcohol group, $-CH_2OH$, while the $-SO_2Cl$ group remained unchanged is based upon the generally accepted assumption that a sulphone chloride is difficult to reduce. That this assumption is not always borne out by experiment is shown by the work of A. Gutmann[1] who reduced toluenesulphone chloride to the corresponding sulphinic acid with a mild reducing agent (sodium arsenite in alkaline solution) and by Davis and Smiles[2] who reduced the dichloride of *m*-carboxybenzenesulphonic acid to *m*-carboxybenzenesulphinic acid by the action of sodium sulphite.

Of all the reactions studied the only one that yields one and only one different product for each chloride is the re-

[1] Ber. d. chem. Ges., **42**, 480.

[2] J. Ch. Soc., **97**, 1925.

duction reaction. This suggests the idea that during the reactions one chloride is converted into the other. Numerous attempts have been made to convert one chloride into the other, but all of these failed until Dr. C. A. Rouiller, working with Professor Remsen, in this laboratory in 1914, made the observation that just as the low-melting phthalyl chloride was converted by Ott[1] into the high-melting phthalyl chloride by the action of aluminium chloride, so, when the high-melting chloride of orthosulphobenzoic acid is mixed with aluminium chloride and warmed to 40°, it is converted quantitatively into the low-melting chloride. This explains why benzene and aluminium chloride yield the same product with both chlorides, as there is opportunity for the aluminium chloride to convert one of the chlorides into the other before the main reaction begins.

At the suggestion of Professor Remsen I have undertaken a study of the action of toluene in the presence of aluminium chloride upon the two isomeric chlorides. It was thought by him that toluene, because of its more reactive nature, would give better results and more easily replace the chlorine atoms than benzene. I have also performed experiments in which the toluene was replaced by benzene. The following pages give the results of this work.

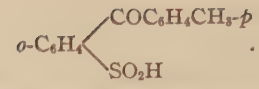
ACTION OF TOLUENE IN PRESENCE OF ALUMINIUM CHLORIDE UPON LOW-MELTING CHLORIDE.

A flask containing a solution of the low-melting chloride dissolved in toluene was packed in a freezing mixture of salt and ice. When the temperature had reached —10°, freshly resublimed aluminium chloride was added in the proportion of two molecules to each molecule of the chloride. Hydrochloric acid gas was evolved immediately and the solution turned dark yellow. After a few minutes the reaction stopped and would not begin again at normal pressure unless the flask was warmed to room temperature. It was undesirable to raise the temperature because of the possibility of

[1] Ann., 392, 274.

the aluminium chloride converting the chloride into its isomer at a higher temperature. Verley[1] found that the Friedel-Crafts reaction with aluminium chloride could be carried out, in general, at lower temperatures if the pressure was diminished. Accordingly, an experiment was tried of diminishing the pressure in the flask in order to draw off the hydrochloric gas as soon as it was formed and thus facilitate the reaction. For this purpose the flask was fitted with a stopper, through which was passed a calcium chloride tube to protect the reaction mixture from moisture, and the calcium chloride tube was connected with a suction pump which diminished the pressure to 30 to 40 mm. As the pressure diminished, the reaction proceeded again vigorously for about a half hour and then quieted down to a slow bubbling. The flask was left thus under diminished pressure over night, and the freezing mixture was allowed to melt slowly and the temperature to rise to about 20°. The flask contained a brown, partly crystalline solid at the bottom upon which was a clear layer of toluene. Pieces of ice were added to dissolve out the excess of aluminium chloride. A light colored mixture of oil and water resulted. This was acidified with hydrochloric acid. Immediately a precipitate was formed which formed a coagulum with the toluene and remained suspended in the water. The precipitate was filtered off and the toluene pressed out in the funnel. It was dissolved in a large volume of very dilute sodium carbonate and reprecipitated with hydrochloric acid as a voluminous white powder. This was easily soluble in alcohol, difficultly soluble in ether, difficultly soluble in cold water, but more easily soluble in hot water from which it crystallized in fine white needles. The yield was about four grams for five grams of the chloride. A dilute water solution of the substance showed an acid reaction, turning blue litmus red, effervescing with a carbonate, and being reprecipitated by acid from the solution in the carbonate. The purified substance did not give a sharp melting point but melted with decomposition when heated at 100–102°. Its reactions and analyses, which will be further described below, showed it to be a compound of the structure

[1] Bull., [3] **17**, 206.



And hence we have called it para-methylbenzoylbenzene-orthosulphinic acid.

Analyses:

I. 0.1979 gram of the substance gave 0.0837 gram H_2O and 0.4686 gram CO_2.

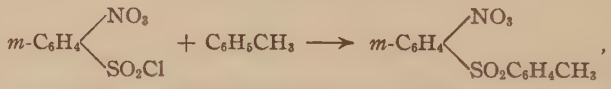
II. 0.1944 gram of the substance gave 0.0811 gram H_2O and 0.4590 gram CO_2.

III. 0.2394 gram of the substance gave 0.2120 gram $BaSO_4$ (Carius).

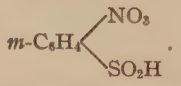
IV. 0.2329 gram of the substance gave 0.2101 gram $BaSO_4$ (Carius).

	Calculated for $C_6H_4\langle^{COC_6H_4CH_3}_{SO_2H}$.	Found.			
		I.	II.	III.	IV.
C.....	64.61%	64.57	64.38	...	...
H.....	4.61%	4.69	4.63	...	...
S.....	12.30%	...	...	12.16	12.38

That a sulphinic acid group should be formed from a sulphone chloride by the action of aluminium chloride and toluene is surprising because it seems to involve a reduction without a reducing agent. However, the formation of a sulphinic acid in this manner is not a new observation. Limpricht[1] in attempting to make *m*-nitrophenyltolylsulphone by the action of toluene in the presence of aluminium chloride upon *m*-nitrobenzenesulphone chloride according to the equation



failed to get the desired sulphone and obtained instead *m*-nitrobenzenesulphinic acid,



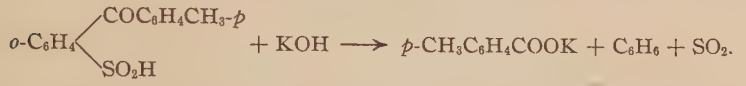
In a similar way, Olivier[2] obtained para-bromsulphinic acid by the action of aluminium chloride and benzene upon para-brombenzenesulphone chloride.

[1] Ann., 278, 256.

[2] Rec. trav. chim., 33, 137 (1914).

Fusion of p-Methylbenzoylbenzeneorthosulphinic Acid with Potassium Hydroxide.

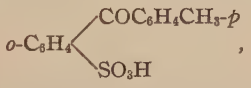
When *p*-methylbenzoylbenzeneorthosulphinic acid is fused with potassium hydroxide it splits up into para-toluic acid, sulphur dioxide, and benzene, according to the equation



The para-toluic acid was identified by its melting point, the melting point of a mixture of the substance with pure para-toluic acid, its solubilities, and the manner in which it sublimed. This reaction shows that the toluene group is in combination with the carbonyl carbon atom.

Action of Water at a High Temperature upon p-Methylbenzoylbenzeneorthosulphinic Acid.

In general, when a sulphinic acid is heated with water in a sealed tube, it yields the corresponding sulphonic acid together with a disulfoxide.[1] When the sulphinic acid under discussion was heated with water in a sealed tube for two hours at 150°, it yielded an extremely soluble strong acid together with another product which is probably a disulfoxide, but whose composition has not been studied for lack of time. The properties of the acid identified it as the *p*-methylbenzoylbenzeneorthosulphonic acid,



which Krannich[2] first prepared by the action of toluene and aluminium chloride upon the anhydride of ortho-sulphobenzoic acid.

Potassium Salt.—This salt made by neutralizing with potassium hydroxide the acid obtained by decomposing the sulphinic acid in a sealed tube with water at 150°, crystallized in thick prisms, such as Krannich describes. It melted sharply at 248°. It gives off its water of crystallization below

[1] Otto: Ber. d. chem. Ges., 10, 2181.

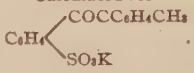
[2] Ber. d. chem. Ges., 33, 3485.

110°. An analysis showed it to have the composition, $C_{14}H_{11}O_4SK.H_2O$.

Analysis:

I. 0.2494 gram of the anhydrous salt gave 0.0703 gram K_2SO_4.
II. 0.2634 gram of the hydrated salt lost 0.0141 gram H_2O.

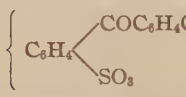
Calculated for



		Found.
K.....	12.45%	12.65
H_2O.....	5.42%	5.33

Barium Salt.—This salt was made by boiling the acid with barium carbonate, filtering, and evaporating to dryness. We were unable to get the small amount of this salt, which we made, to crystallize as Krannich did. The purity of the substance, however, was attested by the fact that it melted at the same temperature, 215°, as his salt, and also by its analysis.

0.3115 gram of the substance gave 0.1041 gram $BaSO_4$.



Calculated Ba.... 19.43%

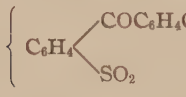
Found..... 19.66%

Ammonium Salt.—This was made by neutralizing the acid with dilute ammonia, and was found to crystallize from a very concentrated solution. The crystals melted at 103.5°, whereas those of Krannich melted at 104°.

Salts of p-Methylbenzoylbenzeneorthosulphinic Acid.

Barium Salt.—Attempts to get the barium, calcium, and ammonium salts in crystalline form failed. The solutions of the salts yielded only syrups when evaporated. From the syrup, by evaporating to dryness, a fairly pure barium salt was obtained as is shown by the following analysis:

0.3660 gram of the substance gave 0.1284 gram $BaSO_4$.



Calculated Ba.... 20.96%

Found..... 20.64%

Magnesium Salt.—This salt crystallizes from its water solution in flat, rhombic plates which melt sharply at 58°.

It contains an unusually large amount of water of crystallization, is efflorescent and gives off all of its water below 110°.

I. 0.24565 gram of anhydrous substance gave 0.0185 gram MgO.
II. 0.24565 gram of anhydrous substance gave 0.0185 gram $MgSO_4$.

Calculated for $\{C_6H_4(COC_6H_4CH_3)(SO_2)\}_2Mg$	Found.	
	I.	II.
4.48% Mg	4.53%	4.55%

Zinc Salt.—This salt was made by boiling a solution of the sulphinic acid with zinc oxide. It crystallized in flat plates from its water solution, and these melted sharply at 49°. It contains a large amount of water of crystallization and is efflorescent when exposed to the air.

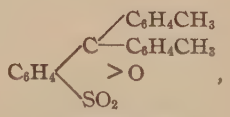
Cadmium Salt.—This salt was made by boiling a solution of the sulphinic acid with cadmium carbonate. It crystallized from its water solution, but the crystals were not of good form. They melted at 140°.

ACTION OF TOLUENE IN THE PRESENCE OF ALUMINIUM CHLORIDE UPON THE HIGH-MELTING CHLORIDE.

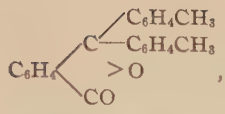
In the first experiment tried the high-melting chloride was mixed in a flask with aluminium chloride in the proportion of two molecules of the latter to one of the former, and the mixture which melted together and became warm, was cooled in ice water. To this was added toluene which had been previously cooled in ice water. Reaction took place slowly with the evolution of hydrochloric acid gas. The pressure was then diminished as in the experiment with the low-melting chloride. After the reaction was over the mixture was treated with ice and hydrochloric acid in the same way as the reaction mixture of the low-melting chloride. The same product, para-methylbenzoylbenzeneorthosulphinic acid, was obtained. We concluded that the aluminium chloride, when mixed with the high-melting chloride, had converted it into the low-melting chloride before it could react with the toluene, and it was in reality the low-melting chloride which had reacted to give the sulphinic acid.

To test this view we tried to work under conditions such that the aluminium chloride would not have a chance to change the high-melting chloride into its isomer before the toluene reacted with it. The result of the experiment showed that our conclusion was correct.

The high-melting chloride was dissolved in toluene and the solution cooled in a freezing mixture to —10°. To this aluminium chloride was added in the proportion of two molecules for each molecule of the chloride. A very slow reaction began but stopped in a minute or two. As in the case of the experiment with the low-melting chloride, the flask was connected with a vacuum pump and allowed to stand over night under the same conditions as to temperature and pressure. The reaction mixture was treated with ice and hydrochloric acid, shaken well, and allowed to stand a half hour. It then consisted of two layers, a water layer at the bottom and a very dark colored toluene solution above. The layers were separated. The water solution was found to contain practically no organic material. The toluene layer was dried over calcium chloride and evaporated to solidification under diminished pressure by bubbling dry air through it several days. This method of evaporation is important because when the toluene is evaporated by heating only a tarry mass remains from which practically nothing definite can be obtained. The solid material was dissolved in warm alcohol. The solution was colored very dark, almost black. Upon digesting several times with animal charcoal most of the coloring matter was removed. Colorless crystals separated from this solution upon standing. These, when recrystallized, melted at 132°. From its analysis and its reactions towards alkalies we were led to the belief that the compound has the structure

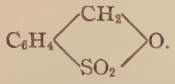


which is analogous to ditolylphthalid,



which has been made by Berchem[1] by the action of toluene and aluminium chloride upon phthalyl chloride.

We, therefore, call the substance ditolylorthosulphobenzid, regarding it as a derivative of sulphobenzid,



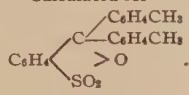
It should be stated that the study of the substance has not been completed and further evidence is necessary before a definite statement as to its structure can be made.

Analysis:

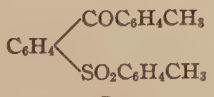
I. 0.2193 gram of the substance gave 0.0987 gram H_2O and 0.5763 gram CO_2.

II. 0.2782 gram of the substance gave 0.1249 gram H_2O and 0.7343 gram CO_2.

III. 0.1921 gram of the substance gave 0.1262 gram $BaSO_2$ (Carius).

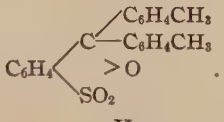
	Calculated for 	Found.		
		I.	II.	III.
C.....	72.00%	71.66	72.11	....
H.....	5.14%	4.94	4.98	....
S.....	9.14%	...	...	9.02

The analyses show that the compound is a result of replacing the two chlorine atoms of the original chloride with two tolyl groups. There are, then, two possibilities. The compound may be



I.

or



II.

An alkali would split up the sulphone of Formula I into paratoluic acid and tolylphenylsulphone, whereas it would open

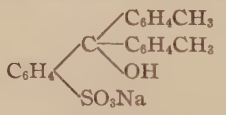
[1] Bull., 42, 168.

up the lactone ring of the second and form a salt in the following manner:

When fused with potassium hydroxide or with sodium hydroxide, or when boiled with a solution of these reagents, a salt is formed which has a rich purple color. A small amount of this salt dissolved in a large volume of water imparts a beautiful, permanganate-like purple color to it. If an acid is added the color is destroyed and a colorless substance is precipitated. When this substance is boiled again with an alkali it gives back the purple salt. We do not yet know what the substance precipitated by an acid is.

When allowed to stand or when boiled for a long time, a water solution of the purple salt undergoes a change, gradually losing its color. For this reason it has as yet been impossible to get the salt in pure condition for analysis. An analysis of the impure sodium salt indicated that it contains one and only one atom of sodium.

0.3558 gram of the substance gave 0.0739 gram of sodium sulphate or 6.7% of sodium. The calculated amount for

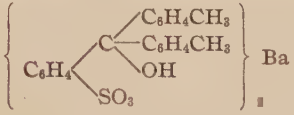


is 5.8% sodium.

If barium chloride is added to a solution of the sodium salt a purple barium salt is precipitated which is insoluble in water and also in every organic solvent at our disposal. The barium salt, however, when allowed to stand in water or when boiled for a long time undergoes a change similar to the sodium salt, loses its color, and goes partly into solution. From this solution an acid precipitates a substance similar to that precipitated from the solution of the sodium salt. A purer barium salt was obtained by boiling the ditolylsulphobenzid directly with a solution of barium hydroxide for two hours. The salt stuck to the bottom of the flask. It was

removed with a spatula, washed, dried and submitted to analysis.

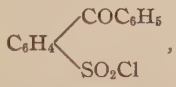
0.2840 gram of substance gave 0.0762 gram barium sulphate or 15.79% barium. The calculated amount for



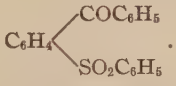
is 15.75%.

ACTION OF BENZENE AND ALUMINIUM CHLORIDE UPON THE CHLORIDES.

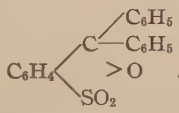
In 1895, Remsen and Saunders[1] studied the action of benzene and aluminium chloride upon the chlorides and found that when the reaction took place at a low temperature ortho-benzoylbenzenesulphone chloride,



was formed from both the high- and low-melting chlorides. At higher temperatures both chlorides gave ortho-benzoyldiphenylsulphone,



A mixture of the two chlorides was found to give mainly the last-named compound and also a very small amount of an unsymmetrical compound of the structure,



Since that work, numerous attempts to get this compound by the action of benzene and aluminium chloride upon a single chloride have failed. Fritsch[2] obtained it by the action of benzene and aluminium chloride upon a mixture of the chlorides. List and Stein[3] obtained it in the same way.

[1] Am. Ch. J., 17, 354.

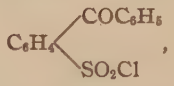
[2] Ber. d. chem. Ges., 29, 2295.

[3] Loc. cit.

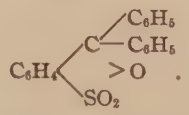
Cobb[1] obtained it by the action of magnesium phenyl bromide upon the anhydride of ortho-sulphobenzoic acid, and[2] by the action of this reagent upon the low-melting chloride. But, as Cobb points out, this reaction cannot be considered as evidence for the structure of the chloride for we are not justified in saying that the phenyl groups of the reaction product occupy the positions of the chlorine atoms in the original chloride.

If the unsymmetrical compound could be formed by the action of benzene and aluminium chloride upon one of the chlorides we should have very strong evidence that that chloride had the unsymmetrical structure. The fact that toluene had given an unsymmetrical product when the reaction took place in the cold under diminished pressure led to the hope that under similar conditions benzene would yield an unsymmetrical product with one of the chlorides.

The experiment was tried upon both the high- and low-melting chlorides in exactly the same manner as has been described for the reaction of toluene and the chlorides in the presence of aluminium chloride, except that the temperature was kept at the melting point of benzene. The low-melting chloride yielded only the benzoylbenzenesulphone chloride,



whereas the high-melting chloride yielded the same substance in large part, but also a small amount of a product whose melting point (163°) and reactions with alkali showed it to be the unsymmetrical diphenylorthosulphobenzid,



The experiment was repeated a second time with the same results.

[1] Am. Ch. J., **35**, 486.
[2] Ibid., **45**, 605.

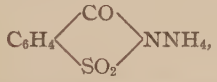
CONCLUSIONS.

This investigation has shown that the low-melting chloride of ortho-sulphobenzoic acid yields a symmetrical product with both toluene and benzene in the presence of aluminium chloride. It has shown that the high-melting chloride with the same reagents yields products whose properties can best be explained by regarding the chloride as an unsymmetrical compound.

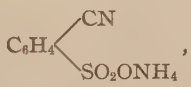
The results are directly contrary to the view thus far held by most chemists, that the high-melting chloride has a symmetrical structure and the low-melting chloride an unsymmetrical structure. This makes it advisable to consider as briefly as possible the various lines of evidence that have been presented.

In support of the symmetrical structure for the high-melting chloride and the unsymmetrical structure for the low-melting chloride we have:

1. The reactions of ammonia with the two chlorides yielding ammonium benzoicsulphinide,

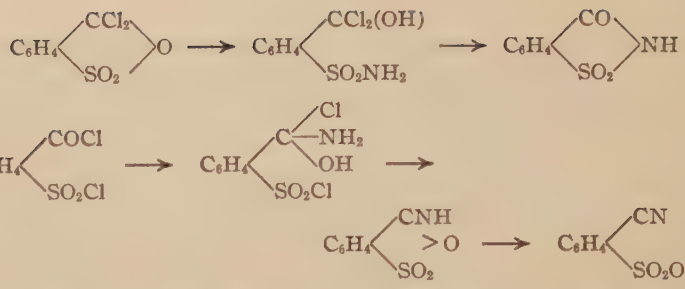


with the high-melting chloride, and mainly ortho-cyan-benzenesulphonic acid,



with the low-melting chloride. This is the strongest evidence in support of this side of the question; and yet we do not have here a case which gives clear evidence for the position of the chlorine atoms in the chlorides. We do not know by what process the sulphinide or the cyan-sulphonic acid is formed. Indeed, as Scheiber and Knothe[1] have pointed out, it is conceivable that the sulphinide should come from an unsymmetrical compound and the sulphonic acid from a symmetrical compound by processes which may be represented in the following way:

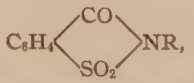
[1] Scheiber and Knothe, Ber. d. chem. Ges., **45**, 2252; Scheiber, Ibid., **46**, 2366.



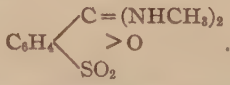
2. The reactions with aniline resulting in the formation of two isomeric anilides has been offered as evidence. That two isomeric compounds are obtained which must be represented by the formulas:

is proved beyond doubt, but the only evidence offered that the fusible anilide has the symmetrical and the infusible the unsymmetrical structure is that they come from chlorides which are believed to have the symmetrical and unsymmetrical structure, respectively. It would now be reasoning in a circle to base the structure of one of the chlorides upon the symmetrical or unsymmetrical anilide which it yields.

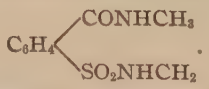
3. As regards the action of the amines upon the chlorides, the point brought out is that the low-melting chloride yields in addition to the ester of benzoic sulphinide,



which the high-melting chloride also yields, an infusible unsymmetrical diamide,



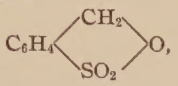
Here again no proof is given that the diamide has the unsymmetrical structure and is not the symmetrical diamide,



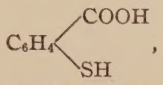
What is the evidence in favor of the symmetrical structure

for the low-melting and the unsymmetrical structure for the high-melting chloride?

(1) With reducing agents the high-melting chloride gives a compound, sulphobenzid,



which may be regarded as the unsymmetrical chloride in which two chlorine atoms are replaced directly by hydrogen. The low-melting chloride gives a symmetrical product, thiosalicylic acid,



which can better be explained as a product of a symmetrical than of an unsymmetrical compound.

(2) With toluene the low-melting chloride yields a symmetrical product and the high-melting chloride gives a compound whose reactions indicate that it has an unsymmetrical structure.

(3) With benzene and aluminium chloride, the low-melting chloride yields only symmetrical products. The high-melting chloride is converted by aluminium chloride into the low-melting chloride. If precautions are taken to prevent this conversion as far as possible, the high-melting chloride yields in addition to the symmetrical product a small amount of what is, in all probability, an unsymmetrical product.

(4) The fact that the low-melting chloride shows light absorption of the same nature as the acid itself, while the high-melting chloride is much more transparent, indicates that the low-melting chloride has the symmetrical and the high-melting chloride the unsymmetrical structure.

In conclusion, it may be stated that, although the problem has not been solved, the facts which have been established up to the present time in connection with the two isomeric chlorides of ortho-sulphobenzoic acid point most strongly to the symmetrical structure for the low-melting chloride and the unsymmetrical structure for the high-melting chloride.

JOHNS HOPKINS UNIVERSITY,
May, 1915.

BIOGRAPHY.

Marion Byrd Hopkins was born at West River, Maryland, June 24, 1889. He moved to Baltimore in 1899. His elementary education was received in the public schools of that city. After being graduated from the Baltimore City College in 1908, he entered the Johns Hopkins University as an undergraduate student. He received the degree of Bachelor of Arts in June, 1912. He has pursued graduate studies in chemistry at the same institution for three years. During the past year he has been lecture assistant to Professor J. E. Gilpin.